Structure and Dynamics of Associative Polymer Gels

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Abstract

Associative polymers have attracted wide attention for applications spanning biomedicine, soft robotics, and rheological modification due to their unique viscoelastic and stimuli-responsive properties imparted by their dynamic bonds. However, predicting the response of associative polymer networks remains a challenge due to the interplay between chain and bond dynamics on various timescales, which governs their properties such as self-diffusion, relaxation, and creep.

In this thesis, a combined experimental and computation approach was used to provide new insight into the structure and dynamics of associative networks on various length and time scales, with the goal of understanding effects of key molecular parameters on their macroscopic behavior. The first part of this thesis studied molecular relaxation and self-diffusion of a model associative network formed by artificial coiled-coil proteins with a well-defined architecture. The combination of forced Rayleigh scattering (FRS) and neutron spin-echo (NSE) spectroscopy provided evidence for several regimes of gel relaxation behavior across a wide length scale range, including subdiffusive caging and two distinct regimes of apparent superdiffusion before terminal Fickian diffusion. The submolecular relaxation dynamics were further probed by varying the strand length and chain concentration, illustrating changes in segmental motion that reflected the underlying network design. Importantly, segmental relaxation rates were found to collapse onto a master curve when rescaled by the static inter-junction spacing measured by neutron scattering, indicating self-similar dynamics even in networks with different chain architecture and concentration. Furthermore, the presence of two distinct superdiffusive regimes on intermediate length scales suggested the existence of multiple origins for anomalous diffusion in associative systems, reflecting a complex interplay between distinct molecular states not captured by current theories.

To obtain further insight into the molecular mechanisms underlying associative network dynamics, a coarse-grained bead-spring model was developed and implemented via Brownian dynamics simulations. Associative polymers were conceptualized as linear chains containing regularly spaced stickers interacting with a mean-field background, obviating the need to explicitly model multi-chain interactions and reducing computational cost. The simulations demonstrated the coexistence of multiple diffusive modes, termed walking and hopping, that give rise to the superdiffusive behavior seen experimentally. Importantly, the two superdiffusive regimes were found to occur by distinct mechanisms, with the lower regime occurring due to a transition between multiple walking modes (irrespective of the hopping mode) and the upper regime occurring due the onset of molecular hopping. Molecular hopping was shown to be important only in kinetics-limited systems, where the sticker association/dissociation dynamics are slower than the intrinsic Rouse relaxation of the network strands. The simulations were also used to probe the effects of molecular parameters such as the sticker density, chain concentration, and association/dissociation kinetics on self-diffusion. Notably, the results demonstrated the importance of loops in enabling chains with high sticker density to hop, whereas the mean-field prediction of purely Fickian diffusion of all length scales was recovered at high chain concentration where the hopping mode was effectively suppressed. Analytical theories were formulated to predict the characteristic walking and hopping diffusivities from the chain topological statistics and dissociation/association timescales, finding qualitative agreement with simulation.

Finally, the last part of the thesis explored the possible contribution of multi-chain correlations toward network dynamics on different length scales, effects that are not captured by single-chain conceptualizations commonly used. Structural characterization of a model associative protein gel using small-angle and ultra-small-angle neutron scattering provided evidence for a previously unobserved static correlation length larger than the inter-junction spacing, indicating inhomogeneity in the chain density distribution in the gel. Self-diffusion measurements suggested a caging effect induced by this large-scale correlation length in governing a transition between distinct slow and fast diffusive modes. Finally, a comparison to the single-sticker dissociation time inferred from tracer diffusion measurements supported the single-chain mechanisms of walking and hopping as previously conceptualized, with the step size of the slow mode commensurate with the length of the bridging strands and the transition timescale to the fast mode consistent with the onset of hopping via dissociation of all stickers on a chain.

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